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THE OXIDATION OF AMMONIA
(Critical Survey)

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MICROMEDIA

THE OXIDATION OF AMMONIA
(Critical Survey)

by

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ABSTRACT

This literature survey provides a brief account of oxidative decomposition of ammonia and ammonium salts with oxygen (O_2), ozone (O_3), hydrogen peroxide (H_2O_2), by alkaline breakpoint chlorination (OCl^-), SO_2-O_2 mixture, electrooxidation and photocatalyzed oxidation. The processes of electrooxidation, hypochlorite and breakpoint chlorination oxidize NH_3-N to nitrogen (N_2); whereas O_2, O_3, H_2O_2 and metal oxide catalyzed oxidation lead to the formation of nitrite (NO_2^-) and nitrate (NO_3^-). Oxidative decomposition of cyanide, an ammonia precursor with H_2O_2, OCl^- and SO_2-O_2 mixture has been briefly discussed. The advantages and disadvantages of these oxidation processes have been discussed briefly. Finally, several R&D recommendations have been put forward for the control of ammonia in mine-mill effluents.

Keywords: Ammonia, oxidation, decomposition, ammonia control

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INTRODUCTION

Ammonia is an important industrial chemical and always is present in air and natural water in trace amounts. Industrially, ammonia is synthesized from gaseous nitrogen and hydrogen at high temperature, under pressure and in the presence of a suitable catalyst (Eq 1) (1). Currently anhydrous ammonia is available at a cost of (U.S.) $ 160.0/tonne (2).

$$N_2 + 3H_2 \rightharpoonup 2NH_3 \qquad (1)$$

The occurrence of ammonia gas and/or ammonium salts in mine-mill operations is a common phenomenon. The majority of ammonia in the mine-mill operations appears due to explosives (ANFO) applied in mining operations, oxidation and hydrolysis of cyanides in gold mills, and ammonia or ammonium salts employed in the recovery of uranium as ammonium diuranate.

Ammonia is a reactive chemical and has various industrial applications. It is a fairly strong base and reacts readily with water and acid, undergoes oxidation, decomposition, complexation with various metal ions and adsorption on inert materials.

At ordinary temperature and pressure ammonia exists as a colourless gas. Both gaseous ammonia and aqueous ammoniacal solutions have a penetrating pungent and suffocating odour. The maximum permissible concentration to human exposure is set at 35 ppm by the US' NIOSH(3); whereas its toxicity is set at 10 ppm of nitrogen as ammonia by Ontario's Ministry of Environment. Lungs, respiratory system and eyes are the primary target organs which are affected by ammonia exposure.

This review provides a brief and critical account of ammonia oxidation with oxygen (O_2), ozone (O_3), chlorine (Cl_2), peroxides (H_2O_2), and electrolytic oxidation, SO_2-O_2 mixture and photocatalyzed oxidation.

Oxidation with oxygen

Ammonia gas burns in air or oxygen with the formation of nitrogen (N_2), oxides of nitrogen (NO_x) and steam (H_2O) (1,4,8,9). Air or oxygen seldom oxidizes an aqueous solution of ammonia unless nitrifying bacteria are present. Most nitric acid is manufactured by oxidizing gaseous ammonia with air or oxygen at high temperature (>600°C) and in the presence of a metal catalyst such as Pt, Pt-Ir or Pt-Rh (Eq 2-5).

$$2NH_3 + {}^3/_2\, O_2 \rightharpoonup N_2 + 3H_2O \quad (2)$$

$$2NH_3 + {}^5/_2\, O_2 \rightharpoonup 2NO + 3H_2O \quad (3)$$

$$2NO + {}^1/_2\, O_2 + H_2O \rightharpoonup 2HNO_2 \quad (4)$$

$$2HNO_2 + O_2 \rightharpoonup 2HNO_3 \quad (5)$$

Oxidation with ozone

Ozone, a triatomic allotrope of oxygen is one of the strongest commercially available oxidant. Ozone itself is a toxic gas. Because of its strong oxidizing and bactericidal properties ozone is finding an increasing application in the treatment of waste waters (7).

Ozone is prepared by passing dry air or oxygen through a high voltage electric discharge. Both gaseous ammonia and aqueous ammonia can be oxidized with ozone. The final oxidation product is nitrate (Eq 6-9).

$$3NH_3 + 3O_3 = 3HNO_2 + 3H_2O \quad (6)$$

$$3HNO_2 + O_3 = 3HNO_3 \quad (7)$$

$$3NH_3 + 4O_3 = 3HNO_3 + 3H_2O \quad (8)$$

$$3NH_4^+ + 5O_3 = 3NO_3^- + 6H_2O \quad (9)$$

Ozone consumption per mole of ammonia and ammonium ion according to equations 8 and 9 are 1.33 and 1.67 moles respectively. It is reported in the literature

that the oxidation rate of ammonia or its salts in the aqueous medium is accelerated with the presence of bromide ion or a catalyst (5-7).

Commercial generators can produce ozone at a rate of 68 kg - 363 kg per day from air and 150 kg - 900 kg per day from oxygen with conversion efficiencies averaging 1.5% from air-feed and 3.0% from oxygen feed operations. The power consumption for generating ozone averages 14.3 kWh/kg from air feed and 7.0 kWh/kg from oxygen feed operations. In the treatment of mine-mill effluents ammonia is not the only ozone consumer. Others are chemical species susceptible to oxidation. Because of this it is advisable to optimize ozone consumption for the treatment of specific effluents.

Oxidation with peroxides

Hydrogen peroxide (H_2O_2) metal oxides such as PbO_2, Co_2O_3, MnO_2 or Fe_2O_3; persalts such as $K_2S_2O_8$, $KMnO_4$ oxidize both ammonia and ammonium salts. The principal products are nitrite and nitrate (4,8) (Eq 10-12). So far no report is available in the literature on commercial oxidation of ammonia or ammonium salts with peroxides.

$$2NH_3 + 7H_2O_2 = 2NO_2^- + 10H_2O \quad (10)$$

$$2NH_3 + 9H_2O_2 = 2NO_3^- + 12H_2O \quad (11)$$

$$2NH_4^+ + 10H_2O_2 = 2NO_3^- + 14H_2O \quad (12)$$

On the basis of these oxidation reactions hydrogen peroxide (H_2O_2) requirements are 3.5 and 4.5 moles respectively per mole of ammonia for oxidation to nitrite and nitrate (Eq 10 and 11). Whereas 5 moles of H_2O_2 would be necessary for the oxidation of 1 mole of ammonium nitrogen into nitrate (Eq 12). The cost of hydrogen peroxide varies from (U.S.) \$0.54/kg of 35% reagent to \$1.08/kg of 70% (2). A solution effluent containing 100 ppm N^+H_4 (i.e. 100 g N^+H_4/m^3) would require 1350 g of H_2O_2 of 70 wt% for oxidation to nitrate at a cost of (Cdn) \$1.63/m^3.

Oxidation with halogen

Gaseous ammonia burns in chlorine with the formation of nitrogen trichloride (NCl_3) which is a highly explosive product. Even ammonium salt reacts with chlorine (dry reaction) and forms nitrogen trichloride (4,9) (Eq 13,14).

$$NH_3 + 3Cl_2 \rightharpoonup NCl_3 + 3HCl \quad (13)$$

$$NH_4Cl + 3Cl_2 \rightharpoonup NCl_3 + 4HCl \quad (14)$$

Pressley et al. invented the breakpoint chlorination process for oxidation of dissolved ammonia in waste water (10,11). Chlorine was applied in the gaseous state to a stream of water and base before mixing with the waste water - in a breakpoint reactor. Chlorine is added to process water until a point is reached where the total dissolved chlorine has reached a minimum concentration level (the breakpoint) when NH_3-N has disappeared.

In the breakpoint reactor HOCl is the principal oxidant which oxidizes NH_4^+-N into various chloramine products (Eq 15-19). Dichlor and trichloramines are formed under acidic conditions. The favoured reactions (Eq 15,19) take place in a pH range of 7.0-8.5. EPA's studies indicated that Cl:NH_4^+-N weight ratio at breakpoint chlorination varied from 8:1 to 10:1 (10-13). Because of the high chemical reactivity of chlorine, there is always some non-ammonia chlorine demand. As a result the total chlorine demand for the breakpoint operation may go as high as 15:1 for Cl:NH_4^+-N (12).

$$Cl_2 + H_2O \rightharpoonup HOCl + HCl \quad (15)$$

$$NH_4^+ + HOCl \rightharpoonup NH_2Cl + H_2O + H^+ \quad (16)$$

$$NH_2Cl + HOCl \rightharpoonup NHCl_2 + H_2O \quad (17)$$

$$NHCl_2 + HOCl \rightharpoonup NCl_3 + H_2O \quad (18)$$

$$2NH_2Cl + HOCl \rightharpoonup N_2 + 3HCl + H_2O \quad (19)$$

The breakpoint chlorination is a suitable process for the removal of ammonia from waste water but excessive chlorine consumption, caustic or lime treatment for pH adjustment and the necessary safety measures for handling of corrosive chlorine are all discouraging factors for any commercial application. Beside all these operational disadvantages the reagent costs are fairly high; for example the cost of chlorine alone for treating an effluent containing 100 ppm NH_4^+-N would be (U.S.) \$0.22/m³*; when chlorine consumption is at the ratio of 10:1 by weight for Cl:NH_4^+-N.

Alkaline chlorination is also applied in the oxidation of cyanides in gold mill effluents (Eq 20-23). Cyanate (CNO^-) is an initial oxidation product of cyanide (CN^-, Eq 21). Cyanate could hydrolyse into ammonia and carbon dioxide (Eq 22). However, this hydrolytic reaction of cyanate could be prevented by further oxidation with chlorine under alkaline condition with the formation of nitrogen and bicarbonate (Eq 23).

$$CN^- + Cl_2 = CNCl + Cl^- \quad (20)$$

$$CNCl + 2OH^- = CNO^- + H_2O + Cl^- \quad (21)$$

$$CNO^- + H^+ + H_2O = NH_3 + CO_2 \quad (22)$$

$$2CNO^- + 3Cl_2 + 4OH^- = N_2 + 2CO_2 + 6Cl^- + 2H_2O \quad (23)$$

Alkaline chlorination of the cyanide effluent is an important process for the abatement of ammonia in gold mill effluents. However chlorine consumption is fairly high: 2.5 moles of chlorine per mole of cyanide. As well, strict control of pH at 10.5 or above is necessary for efficient oxidation of cyanide (14). One tonne of a gold effluent solution containing 100 ppm cyanide (CN^-) would cost (U.S.) \$0.15 of chlorine alone. But in practice the chlorine consumption would be much higher due to consumption by the non-cyanide species present in the effluents.

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* chlorine at (U.S.) \$220.0/tonne (2).

Electrooxidation

An aqueous solution of ammonia or ammonium salt can be oxidized anodically into elemental nitrogen without forming any other oxidation products; such as nitrate (NO_3^-), nitrite (NO_2^-), hydrazine ($H_2N\text{-}NH_2$) or hydroxylamine (NH_2OH) (4,15,16). Recent reports in the literature indicate that the anodic oxidation can take place even at a concentration of 2 mg/L ammonia by using a platinum electrode. Marincic and Leitz in 1973 estimated power and capital cost for the removal of 20 ppm ammonia in a waste water with a unit cost of (U.S.) \$7.0/ft^2 of electrode amounted to \$0.46/1000 gallons of water (i.e.; \$0.121/m^3) (16).

Photolysis and photo oxidation

Ultraviolet (UV) light decomposes ammonia into nitrogen and hydrogen (Eq 24); however ammonium nitrate is formed when UV irradiation is conducted on a mixture of ammonia and oxygen (4). Recently the EPA is showing considerable interest in the development of a waste water treatment process based on photocatalytic oxidation of organic and inorganic species (9,17). This photo oxidation process would be based on UV irradiation of waste water with oxygen in the presence of catalytic amount of titanium dioxide (TiO_2). So far no report is available on cost estimates for this process.

$$2NH_3 \xrightarrow{UV} 2N_2 + 3H_2 \qquad (24)$$

Oxidation with Inco SO_2/air process

The Inco SO_2/air process is finding increasing application in the oxidation of cyanides in gold mill effluents. Cyanide (CN^-) is oxidized to cyanate (CNO^-) with the mixture of SO_2-O_2 in the presence of soluble copper which acts as a catalyst (18). Both cyanide and cyanate are ammonia precursors. As an oxidant this mixture is comparable with the oxidation mechanisms of hydrogen peroxide (H_2O_2). So far no report is available in the literature on oxidation of ammonia with SO_2/air mixture. Lately, the

presence of soluble copper in the mill discharge is raising considerable environmental concerns.

Environmental impact of the oxidation processes

The oxidation of ammonia with O_2, O_3 or H_2O_2 forms not only NO_2^- and NO_3^- but also a host of products such as hydrazine (N_2H_4), hydroxyl amine (NH_2OH), tetrazine ($H_2N.NH.NH.NH_2$), nitroso products, salts of hydrazoic acid (1). Many of these species may form stable complexes with the heavy metal ions. Furthermore, ammonia and some of the above species may react with atmospheric carbon dioxide (CO_2) and form ammonium carbonate ($H_2N\text{-}COONH_4$) urea ($OC\text{-}N_2H_4$), metal cyanamids (e.g. $CaCN_2$). Majority of these products are toxic, carcinogenic, ammonia precursors and algal growth promoters.

Similarly the oxidation of ammonia by alkaline chlorination processes (i.e.; breakpoint or OCl^-) yields various chloramines, nitrosyl chloride (NOCl) in addition to various metal chloro salts. Chlorine also reacts with sulphur, sulphide and partially oxidized sulphide and form various sulphur chlorides and nitrides such as S_2Cl_2, SCl_2, SCl_4, $SOCl_2$, S_4N_4 (1). Majority of these products are toxic and chemically highly reactive. However, the formation and concentration of kinds of oxidation and chlorination products largely depends on the process condition, reagent concentration and the initial concentration of ammonia in the feed. Fortunately, majority of these products are not chemically very stable in the aqueous medium.

COMMENTS AND RECOMMENDATIONS

The oxidation processes which lead to decomposition of ammonia or ammonium salts into nitrogen and hydrogen or nitrogen and water would be the most suitable. In this respect electrooxidation, breakpoint chlorination and hypochlorite or hypobromite oxidation processes are notable.

Technologically electrooxidation is a sound process. Its highest oxidation rates and current efficiency occur with the application of a platinum electrode. Platinum is

one of the most expensive noble metals. The process cost in terms of electrode and power consumption amounted to (U.S.) $0.46/1000 gallons at 1973's prices. However, because of high technological merit of this process, some R&D efforts would be a worthy investment for the development of a cost effective electrode.

Both breakpoint chlorination and hypochlorite oxidation of ammonia or ammonium salt essentially follow the same oxidation mechanism. These oxidation processes are very reagent intensive. Generally chlorine consumption is in the range of 10 to 15 times per weight of NH_4^+-N treated.

Alkaline chlorination process is also being applied in the oxidation of cyanides in gold mill effluents. Initially, cyanide is oxidized to cyanate (CNO^-) which is also an ammonia precursor. However the alkaline chlorination process can oxidize cyanate to N_2 and $CO_2/CO_3^=$ with excess supply of chlorine and strict control of pH at 10.5 or above (Eq 22,23).

Beside high chlorine consumption soluble chloride salt formation is high and lime neutralization is often necessary. Furthermore, aqueous alkaline chlorine is a corrosive oxidant which requires corrosion resistant fabrication materials. Because of these drawbacks the chlorite oxidation process is not always a preferred one.

The oxidation of ammonia or ammonium salts with ozone, hydrogen peroxide, heavy metal oxides or persalts respectively is technologically feasible. In fact ozone and hydrogen peroxide oxidation processes respectively are finding increasing applications in the treatment of waste waters. However, NO_2^- and NO_3^- are the main oxidation products and they may cause some environmental concerns especially for the effluents containing high levels of ammonia.

Hydrogen peroxide is finding applications in the oxidation of cyanides in the gold mill effluents; however this oxidation leads to formation of cyanate (CNO^-) which hydrolyses into ammonia (Eq 22). So far no report is available in the literature on the oxidation of cyanate with H_2O_2, O_3 or heavy metal oxides. Table 1 shows some comparative cost data and process status information for various oxidation processes. Although full capital and operating costs are not given for all the options, the values

presented can be used as a basis for comparison of the relative costs of the different options and the total treatment costs which might be anticipated.

Table 1 - Cost Data and Process Status (Feed effluent 100 ppm NH_3)

	Oxidation Process			
	Electrooxidation	Alkaline Chlorination	Ozone	Hydrogen Peroxide
Application Status	Laboratory Scale	Commerical Scale	Commercial Scale	Laboratory Scale
Nature of N Product	N_2	N_2	NO_2^-, NO_3^-	NO_2^-, NO_3^-
Oxidation Efficiency	100%	100%	No data available	No data available
Cost (~1990) (US \$/m^3)	1.44	0.22	0.27	1.63
Items Included in Cost	capital and operating	chlorine only	power only using 0.05/kWh	peroxide only

In view of above survey following recommendations can be put forward for further R&D investigations:

— Ozone would appear to be the most favourable route for chemical oxidation of ammonia. Costs are projected to be substantially lower than with peroxide while no other pollutants such as chloride are introduced into the effluent stream. Research is required to determine whether ozone oxidation on, perhaps with the aid of suitable catalysts, oxidize ammonia to the nitrogen rather than nitrate. The process must also be optimized.

— Cyanide is easily oxidized to cyanate (CNO^-) which too is an ammonia precursor. Oxidation of cyanate to N_2 and CO_2 requires fairly aggressive oxidation condition. In this respect R&D investigations are necessary for the development of a cost effective oxidation process for cyanide (perhaps two stage oxidation process).

— Waste water treatment by photocatalytic oxidation process is now an important R&D issue for EPA; we would be wise to monitor the progress of the development of this process. Perhaps we may conduct R&D investigations in the photocatalytic oxidation of cyanides and ANFO chemicals.

— Electrooxidation of ammonia is a fairly efficient and very clean process. Its economic feasibility substantially depends on the cost of electrode material. Further R&D investigations are necessary for the development of a cost-effective electrode material. At the same time it is worth investigating the feasibility of cyanide destruction by electrooxidation process.

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